Migration of antimony from polyethylene terephthalate used in mineral water bottles

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ABSTRACT

The influence of storage time and temperature on Sb migration from PET bottles into mineral water was studied in short-term tests lasting up to 15 days and long-term studies lasting up to 220 days. Samples purchased were stored in three different coloured bottles: clear (CL), light blue (LB) and dark blue (DB). Sb migration was assayed by HG-AFS for total determination and HPLC-ICP-MS for speciation analysis. Migration studies showed that waters stored at 4 and 20ºC were not subject to Sb migration. At 40ºC there was a significant increase in Sb concentration, although the maximum limit established by the European Union (5.0 μg L^{-1}) was not exceeded, whereas at 60ºC samples were subject to considerable Sb migration after 30 days of storage. In this case, the maximum limit established by the European Union was exceeded and both Sb (V) and Sb (III) were detected.

Keywords: Migration; Antimony speciation; Water; Inductively coupled plasma-mass spectrometry; polyethylene terephthalate bottle.

1. Introduction

In recent decades, bottled water consumption has increased considerably, raising concerns over water quality and the packaging material (Biros, Bridgewater, Villeges-Estrada, Tanski & Parkin, 2002).

Polyethylene terephthalate (PET) is a thermoplastic material that is manufactured for a wide variety of applications, especially food and beverage packaging, including drinking water bottles (Biros et al., 2002; Duh, 2002; Ashby, 1988). The first industrial step in the synthesis of PET is a prepolymerization reaction that generates low-weight oligomers and bis(hydroxyethyl)terephthalate (BHET) as an intermediate compound. A second polycondensation reaction use various catalysts. Of these, antimony trioxide (Sb_2O_3) is widely used because it is efficient, presents a minimal tendency to produce side effects and does not create colour in the polymer (Duh, 2002; Aharoni, 1998). The use of this catalyst can lead to residual Sb contents ranging from 200 to 300 $mg \cdot kg^{-1}$ (Keresztes, Tatár, Mihucz, Virág, Majdik & Záray, 2009; Shotyk, Krachler & Chen, 2006; Shotyk & Krachler, 2007; Tukur, Sharp, Stern, Tizaoui & Benkreira, 2012; Welle & Franz, 2011; Westerhoff, Prapaipong, Shock & Hillaireau, 2008).

Antimony is found as organic and inorganic compounds in two oxidation states. Its other properties, such as solubility and adsorption behaviour, are similar to those of arsenic (Gebel, 1997; Filella, Belzile & Chen, 2002a). Organic antimony compounds are the less toxic forms and between the inorganic forms, Sb (III) is 10-fold more toxic than Sb (V) (Poon et al., 1998; Rivas, López-García & Hernández-Córdoba, 2009; Seiler, Sigel & Sigel, 1988). Therefore, Sb is considered a priority pollutant by the United States Environmental Protection Agency (USEPA) (USEPA, 2009) and the European Union (EU). It has been included in European regulations concerning the quality of water intended for human consumption, among others (Council of the European Union, 1998).

European regulations on plastic materials and articles intended to come into contact with food (European Parliament and the Council of European Union, 2004)) have established specific requirements concerning the substances authorised to be present in these materials, such as monomers, additives, polymer production aids and macromolecules. For these authorised substances, specific migration limits (SML) have been established on the basis of migration tests performed on the plastic material. These tests are based on the risk assessment of the single substance able to migrate, simulating the worst case of the foreseeable conditions, in order to ensure the safety of the final material. Specific migration tests should be carried out directly in food or using different food simulants according to the food type (acetic acid, ethanol, vegetable oil and poly(2,6-diphenyl-p-phenylene oxide)), and different storage times (up to 10 days) and temperatures (5–175 ºC) depending on the foreseen contact time. In PET-packaged food, the SML for Sb_2O_3 is 40 $\mu g \cdot kg^{-1}$ as total Sb (European Comission, 2011).

Studies of total Sb content in drinking waters conducted in recent years have found that although the total residual Sb content is relatively high, the Sb concentration in water samples is well below the Maximum Concentration Levels (MCL) for drinking waters (5 or 6 $\mu g:L^{-1}$) established by USEPA, Canada and the EU, among others (Shotyk et al., 2006; Shotyk et al., 2007; Westerhoff et al., 2008; Cheng, Shi, Adams & Ma, 2010). Such studies concluded that the presence of Sb in bottled water was due to its migration from PET, as fresh water obtained directly from a spring, a well or stored in other types of plastic, such as polypropylene (PP) or low density polyethylene (LDPE), did not contain high Sb levels (Shotyk et al., 2006; Shotyk et al., 2007). Although the influence of PET colour was also studied by several authors, its potential effect remains unclear.

On the one hand, it was reported that there was no correlation between PET colour and the Sb migration potential in more than 40 and 100 water samples analysed (Shotyk et al., 2006; Shotyk et al., 2007; Tukur et al., 2012). On the other hand, Sb migration was found to be higher in water stored in dark coloured bottles than that stored in clear bottles (Reimann, Birke & Filzmoser, 2010), although the opposite effect has also been described when comparing colourless and blue bottles (Westerhoff et al., 2008).

Physicochemical factors that can affect Sb migration from the container to the water have also been studied. Storage time (from 3 months up to 3 years) has been the most studied variable, mainly for samples kept at room temperature. All studies showed that the Sb concentration in mineral water increased over time by 25–90%. However, the maximum concentration limit was not exceeded in any case (Kerestzes et al., 2009; Shotyk et al., 2007; Tukur et al., 2012; Westerhoff et al., 2008).

Other short-term stability studies have examined water samples stored from a few hours to 7 days at temperatures ranging from -20ºC to 80ºC. Whereas a slight increase in Sb content was observed in samples stored at 60ºC, rapid release of Sb into the matrix was observed after 5–24 h of storage at 80ºC. The irradiation of samples with sunlight (either natural or simulated) also caused a small but significant increase in Sb leaching (Kerestzes et al., 2009; Tukur et al., 2012; Westerhoff et al., 2008).

Other factors, such as the presence of carbon dioxide in bottled waters was studied by Bach, Dauchy, Severin, Munoz, Etienne & Chagnon, 2013. Sb concentration in carbonated water was twice as high as non-carbonated water, suggesting that Sb release was accelerated by carbon dioxide.

Other studies have dealt with the total Sb determination in bottled fruit juices and other soft drinks. In these matrices, the reported Sb concentration values were either over or under the maximum level established for drinking waters (Tukur et al., 2012; Hansen et al., 2010).

Few studies have dealt with the identification, quantification and fate of Sb species migrating from PET into beverages. However, the presence of different coordination complexes of Sb (V) has been confirmed, in spiked non-complexed Sb (V) samples of fruit juices stored in PET, using HPLC-ICPMS and HPLC-ES-MS(/MS). The complexes described were of high stability and with different coordination numbers between Sb (V) and citrate, adenosine and lactate. Whereas inorganic Sb (III) or Sb (V)-citrate were the main species present in citrus juices, only non-complexed inorganic Sb (V) was observed in drinking waters, all of them stored in PET (Hansen & Pergantis, 2007). The effect of temperature (50ºC) on the leaching of these species was described for two carbonated and two non-carbonated juices stored for up to 14 days. The leached Sb concentration only increased in carbonated samples and was mainly due to an increase in Sb (III) (Hansen & Pergantis, 2006). Such speciation studies have not been reported for drinking water samples.

In this paper, the influence of various physicochemical factors, including storage time, temperature and PET colour on Sb migration in bottled waters, was investigated. A systematic study was undertaken to assess the effect of storage time longer than 6 months, and storage temperatures from 4ºC to 60ºC on bottled drinking waters. Total Sb and speciation analysis was carried out on water samples bottled in clear and blue PET containers.

2. Materials and methods

2.1. Instrumentation

Microwave digestion of the PET bottles was performed using a Milestone Ethos Touch control instrument, with a temperature controller and a power of 1000 W. For this procedure, twelve Teflon pressure vessels were used simultaneously.

Total Sb content was determined using hydride generation-atomic fluorescence spectrometry (HG-AFS). Hydride generation was performed using a Millennium PS Analytical (Kent-UK), model 10.055. The reagents for stibine generation, HCl 2 mol L^{-1} and $NaBH_4$ 0.7 (w/v) were continuously pumped at 8.0 $mLmin^{-1}$ and 4 mL min^{-1}, respectively. Samples were introduced at 8.0 mL min^{-1}. After reaction in a coil the generated stibine was driven by an argon flow (300mL min^{-1}) to the AFS detector through the type 'ME' gas–liquid separator. Before detection, the argon stream was passed through a Perma pure drying membrane (Perma Pure Products, Farmingdale, NJ, USA) which prevents droplets being transmitted into the transfer line. N_2 was used as drying gas at a flow rate of 2.5 L min^{-1}. Detection was carried out in a P.S Analytical Excalibur Atomic Florescence Spectrometer equipped with a diffusion flame and a Sb-boosted hollow cathode lamp (Super Lamp Photron Teknokroma).

A quaternary pump auto-sampler (Agilent 1200) with an injection volume of between 0.01 and 2000 μL, and an anion exchange column with ammonium quaternary salt and methyl groups as substituents, were used for the separation of Sb species. The outlet of the column was coupled with inductive coupled plasma-mass spectrometry (ICP-MS) (Agilent 7500 ce), with a reaction cell and Burgener Ari Mist HP nebulizer. The ion intensity at m/z 121 (^{121}Sb) was monitored using time-resolved analysis software.

The experimental conditions of HPLC-ICP-MS are the following: PRP-X100 column (125×4.1 mm Hamilton, 10 μm particle size, USA) working at room temperature using 10 mM ethylenediaminetetraacetic acid (EDTA) at pH 4.0 with 0.5% methanol as mobile phase; injection volume of 40 μL; flow rate of 1.5 mL min^{-1}.

2.2. Reagents and standards

The standards and reagents used in this study were prepared with deionized water (Elix&Rios 5–15 M Ω cm^{-1}, Total Organic Carbon <30 μg L^{-1}) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

A 1000 mg L^{-1} stock standard solution of Sb (III) was prepared by dissolving appropriate amounts of potassium antimony (III) oxide tartrate hemihydrate (Fluka, Neu-Ulm, Germany) in water. The solution was diluted to 100 mL.

The 1000 mg L^{-1} stock standard solution of Sb (V) was prepared by dissolving potassium hexahydroxoantimonate (Riedel de-Haën, Seelze, Germany) in water. The solution was diluted to 100 mL.

Both standard solutions were standardised against a certified standard solution of 1000 ± 4 mg L^{-1} of Sb, prepared from metallic antimony 99.999% “purum”, dissolved and stabilised in high purity acids (nitric acid (HNO_3) 5% and hydrofluoric acid (HF) 0.1%).

All stock standard solutions were stored in polyethylene bottles at 4°C. The working standard solutions were prepared daily by dilution in mobile phase for speciation analysis and in acidic medium for total analysis.

For hydride generation in total Sb determination by HG-AFS, sodium borohydride solution was prepared daily from $NaBH_4$ (Aldrich, >97% purity) to a 0.7% concentration containing 0.4% sodium hydroxide prepared from NaOH (Merck, ≥ 99% purity). The HCl solution at 2M was prepared from concentrated HCl (Panreac, hyperpure reagent grade 35%).

Aqueous solutions of the pre-reducing agent in total Sb determination by HG-AFS were prepared daily from both ascorbic acid 99% (Panreac) and potassium iodide, KI, 99.5% (Panreac), at concentrations of 10% and 50%, respectively.

For PET extraction based on end-over-end agitation, a solution of HCl 10 mmol L^{-1} was prepared from concentrated HCl (Panreac, hyperpure reagent grade 35%).

For microwave digestion of PET samples, concentrated HNO_3 (Panreac, hyperpure reagent grade 69%) and sulphuric acid, H_2SO_4, 96% (Merck) were used.

The mobile phase was prepared daily by dissolving EDTA (Panreac) in water. The pH was adjusted with diluted ammonia (Panreac) and then passed through a 0.45 μm filter (Millipore type HA).

2.3. Selection of samples

Three commercial brands of PET-bottled water were purchased in a local market. A previous study screened 38 non-carbonated samples with different degrees of mineralisation and stored in different coloured bottles. The results of this study are summarised in Table S1 as Supplementary Material. No relationship was found between Sb concentration and mineral content. However, more than half of the samples stored in clear bottles contained lower amounts of Sb than those stored in coloured bottles. On this basis, the selection of brands was based of the colour of the PET bottle: clear (CL), light blue (LB) and dark blue (DB). Each brandwas non-carbonated and weak mineralised. Analysis of total Sb and speciation in PET was performed in triplicate for each brand.

Polyethylene certified reference material (CRM) ERM-EC681k from Institute for Reference Materials and Measurements in Geel, Belgium was used for quality control purposes. To our knowledge there are no CRMs for antimony in PET and thus, polyethylene was considered the most similar material to PET available. Antimony certified value for ERM-EC681k is 99±6 mg Sb kg^{-1}.

2.4. Migration experiments

The effect of temperature stress on the Sb concentration in water was also carried out in the three commercial bottled water brands. Total and speciation Sb in water were analysed at the beginning of the test and after 15 days at 60ºC. Samples were then stored for another 15 days at 4ºC and the Sb contents were measured again. The analyses were performed in triplicate in all cases.

The same samples were used to study the influence of storage time and temperature on the Sb concentration in water in long-term migration studies.

Three bottles of each brand were stored at 4, 20, 40 and 60ºC. Speciation and total antimony were analysed by triplicate analysis on 12 occasions until the bottles ran out of water (220 days). The quantification techniques were HG-AFS for total analysis and HPLC-ICP-MS for speciation.

2.5. Determination of antimony in water samples

2.5.1. Total Sb by HG-AFS

A 10 mL aliquote of bottled drinking water was pre-reduced with the ascorbic acid and KI solution in order to achieve the maximum yield of stibine in the hydride generation step and was diluted up to 25 mL in HCl medium. Samples were introduced to the system at conditions mentioned in section 2.1. The samples were quantified by means of an external calibration curve from Sb(III) standards. Analyses in triplicate were performed for each sample. For quality control purposes, the standards of the calibration curve were run before and after each sample series. Quality control standard solutions at two concentrations were measured at the end of the sequence to ensure stable instrument sensitivity.

2.5.2. Speciation Sb analysis by HPLC-ICP-MS

Samples were analysed in triplicate without pre-treatment. A 40-µL aliquot of sample was directly injected into the HPLC system operating at the conditions mentioned in section 2.1. A solution of rhodium was used as the internal standard. The samples were quantified by means of an external calibration curve from Sb(III) and Sb(V) standards. Antimony species in extracts were identified by comparison of retention times with standards. External calibration curves quantified Sb(V) and Sb(III), according to the corresponding standards. All samples were analysed in triplicate. For quality control purposes, the standards of the calibration curve were run before and after each sample series In each speciation run, two quality control standard solutions were measured at the end of the sequence to ensure stable instrument sensitivity. Data acquisition was carried out using ICP-MS Chemstation software, and the peak areas were calculated using the ICP-MS Chromatographic Data Analysis.

2.6. Determination of antimony in PET

2.6.1. Total Sb

PET bottles were cut into pieces measuring 1.0 x 1.0 cm^2, and 0.1500 g of sample was subjected to microwave-assisted closed pre-digestion with 3.0 mL H_2SO_4 at 300 W for 5 minutes. Afterwards the sample was digested with 8.0 mL HNO_3 at 200 ºC for 15 minutes; the samples were filtered through a filter paper (Whatman 40) into a 50-mL flask glass, diluted with de-ionised water and the antimony content of a 10-mL aliquote was analysed as described in section 2.5.1. The corresponding digestion blanks (one for each sample digestion series) were also measured. To assess the accuracy of the method, a CRM (ERM-EC681K) was analysed following the same procedure.

2.6.2. Extraction species

A 1.5-g sample was shaken with 10 mL HCl 10 mM as the extractant solution in Teflon tubes for 16 h at 30 rpm (Miravet, López-Sánchez & Rubio, 2006a). The antimony species in the extracts were determined by HPLC-ICP-MS and total antimony by HG-AFS as described in section 2.5. Extraction blanks were also analysed in each work session. To assess the accuracy of the method, a CRM (ERM-EC681K) was analysed following the same procedure.

3. Results and Discussion

3.1. Antimony in PET material

The concentrations of antimony in the three samples are shown in Table 1. The total Sb content obtained by microwave extraction is included in the first column. Values of Sb species obtained after an HCl extraction together with the total leachable Sb in the extracts are reported in columns 2-4.

Total Sb content was also analysed in polyethylene CRM (ERM-EC681k) providing a concentration value of 101.4±0.2 mg kg^{-1} (n=3) and a RDS of 0.2%. No significance difference was found between certified and experimental total content (dependent t-test for paired samples at 95% confidence level).

As it can be seen in the first column of Table 1, PET bottles contain between 191 and 268 mg kg^{-1} of total Sb, the dark blue sample containing slightly higher levels than the other two samples. The Sb contents measured were comparable with those reported by other authors (154–311 mg kg^{-1}) (Kerestzes et al., 2009; Tukur et al., 2012; Welle et al., 2011; Westerhoff et al., 2008; Takahashi, Sakuma, Itai, Zheng & Mitsunobu; 2008).

The presence of this element in the polymer can be attributed to its use as a catalyst during PET manufacture, as mentioned in the introduction. It can be added as glycolate or antimony trioxide. When it is added as Sb_2O_3, it is readily converted to glycolate (Duh, 2002). At the end of the manufacturing process, Sb remains bound in the polymer chain as antimony glycolate complexes (Duh, 2002; Welle et al., 2011; Takahashi et al., 2008). Nevertheless, it is possible that some Sb_2O_3 remains unconverted (Sánchez-Martínez, Pérez-Corona, Cámara & Madrid, 2013). However, although total Sb in PET is relatively high (up to 300 $mg \cdot kg^{-1}$), the levels of Sb present in beverages in contact with PET are much lower, and there is little information about the migration potential and mechanisms of different Sb chemical forms (Welle et al., 2011).

Therefore, a preliminary test was performed to assess the total Sb and main Sb species extracted from PET. HCl 10 mM was used as the extractant, which after being previously identified as the optimum extractant in other environmental samples (Miravet et al., 2006a). The total HCl-extractable Sb content (second column in Table 1) ranged from 10.0 to 18.2 $\mu g\ kg^{-1}$. Additionally, same experiment was performed on polyethylene CRM providing concentration values of 40.2 $\mu g\ kg^{-1}$. These values corresponded to 0.0037–0.0095% of total Sb in PET, and 0.0396 % in polyethylene sample showing that only a small amount of the antimony present in PET bottles leached into the extractant solution, as indicated by other authors (Welle et al., 2011).

The speciation analysis of HCl extracts for PET samples (third and fourth columns in Table 1) revealed that Sb (V) was the only species present. This is consistent with the results of Takahashi et al. (2008), who concluded that, although antimony is added as a trivalent species during PET manufacture, it can be partially oxidized (up to 50%) to Sb (V). When performing HCl extraction on the polyethylene CRM, 64,9 % of total Sb was present as Sb(III). This different behaviour can be attributed to the procedure described for the preparation of CRM batches, where Sb_2O_3 pigment was added to the polyethylene powder once manufactured. Thus, speciation behaviour of CRM cannot be compared with the PET samples analysed.

As can be seen from the results in Table 1, total Sb content in PET was not directly correlated with the extractable content: light blue samples with the lowest total Sb content showed the highest Sb leachability. Comparison of total Sb extractable content with the speciation analysis (i.e. total Sb versus Sb (V)) via a dependent Student's t-test for paired samples showed statistically significant differences at the 95% confidence level, especially with regard to dark blue bottles. This can be attributed to the small amounts of Sb species found in the measuring extracts, which were close to the limit of quantification where the widespread of expected results can be higher. . Thus there was a significant difference between total extractable contents and species in dark blue bottles.

In order to assess the possible oxidation of Sb(III) during extraction procedure, leaching experiments with addition of 1mL EDTA 10 mM in the extractant solution (HCl 0.01 mol L^{-1}) were performed on LB PET sample. In these extracting conditions, 39 % of total extracted Sb was present as Sb(III). This fact evidenced that the potential Sb(III) form present and extracted from the PET can be easily oxidised to Sb (V).

3.2. Temperature stress test

The potential effect of temperature on Sb release into water during storage was first studied in the short term. The experimental conditions for this study are described in section 2.4. The results are shown in Figure 1, where the total Sb and speciation analyses are plotted for each brand, together with the standard deviation. Accordingly, antimony was detected in all samples before the storage (day 0). Total Sb ranged from

0.3 to 0.7 μg L^{-1}. After storage at 60ºC, a significant increase in total Sb concentration was observed (2.6–4.2 μg L^{-1}). Subsequent storage at 4ºC gave similar values to those obtained after storage at 60ºC.

In the case of speciation studies, Sb (V) was initially the only species present. After 15 days storage at 60ºC, the Sb (V) concentration increased, and Sb (III) appeared in all samples at detectable but not quantifiable levels.

From the reduced number of units analysed, it can be stated that waters stored in coloured bottles contained similar Sb concentrations, but they were slightly higher than those stored in clear bottles. The relative standard deviation ranged from 0.07 to 9.90%. A dependent Student's *t*-test for paired samples, at the 95% confidence level, demonstrated that there was no significant difference between total Sb content and Sb (V). Furthermore, using the same statistical *t*-test it was shown that Sb concentrations after storage at 4ºC did not differ significantly from those previously obtained after storage at 60ºC.

These results showed that, as expected, the exposure of water to a high temperature leads to significant Sb migration from the bottles to the water. It was also observed that antimony is not leached at low temperatures as the Sb concentration remained stable at the lower storage temperature. During these 30 days, there was no change in the Sb species present in water, indicating that they maintained their integrity throughout the experiment. The Maximum Concentration Level (MCL) established by the European Union (5.0 μg L^{-1}) was not exceeded in any case.

Although some consider migration studies at high temperatures (60ºC) to be unnecessary for water samples (Sánchez-Martínez et al., 2013), others have indicated that they are necessary given that the temperatures inside cars, garages and closed storage areas can exceed 65ºC during the summer in some regions (Westerhoff et al., 2008). Thus, based on the results obtained in the short-term stress test, a more systematic study was undertaken.

3.3. Migration study

The effect of different storage temperatures (4, 20, 40 and 60ºC) and times (up to 220 days) on the Sb concentration was assessed. At the beginning of the test, all samples were analysed and Sb (V) was the only species present.

For samples stored at 4°C and 20ºC, a dependent Student's *t*-test for paired samples at the 95% confidence level for the 11 different times assayed showed no significant differences in Sb concentration in water over time. All samples contained total Sb concentrations below 1 µg L^{-1}. Thus, the maximum level established by the European Union (5.0 µg L^{-1}) was not exceeded. The only species present was Sb (V).

The concentrations of total Sb and the results of the speciation analysis from the long-term migration experiments at 40 and 60ºC are summarized in Figures 2 and 3. The first figure shows the total Sb concentration in each brand stored from day 0 to day 220. The second figure shows the Sb (V) concentration under the same conditions.

Samples stored at 40°C showed a significant increase in antimony concentration after 15 days of storage. From 50 days, this increase became quite pronounced and Sb (III) was also detected in light blue and dark blue bottled samples at concentrations below the limit of quantification. However, Sb (III) was not detected from day 97 onwards. The regulated level was not exceeded in any case.

Samples stored at 60°C showed a significant increase in total antimony concentration from the first day of storage. The dark blue samples began to exceed the limit for Sb according to the European Union (5 µg L^{-1}) after 15 days, and after 30 days, all samples exceeded the limit. This is consistent with the results obtained by Kerestzes et al., (2009), Tukur et al. (2012) and Westerhoff et al. (2008) regarding the increase in total Sb concentration in water samples stored at 60ºC for a few hours to 7 days. As far as the PET colour is concerned, the results obtained in this study seem to indicate that Sb release was slightly lower in non-coloured bottles than in coloured ones, regardless of the colour intensity. This is consistent with Shotyk et al. (2007) and Tukur et al. (2012), who reported that there was no correlation between PET colour and Sb migration potential.

Speciation analysis of the samples at 60ºC showed that Sb (III) was detected from the third to the fiftieth day. After day 50, the concentration of this species was slightly above the limit of quantification in clear and light blue samples but clearly higher in dark blue samples. Chromatograms obtained from a water sample stored at 60°C are shown in Figure 4. The insert shows the Sb (III) peaks obtained at day 0 and 7, in which the species could not be quantified. The Sb (III) concentration in samples stored for longer than 50 days is summarized in Table 2. As shown, the amounts of trivalent antimony species were similar from day 68 to day 78 and, from day 78 to 220, it decreased slightly or even disappeared (LB samples). As an internal quality control check, a mass balance comparing the sum of species and total antimony was carried out. A dependent Student's *t*-test for paired samples (95% confidence level) proved that there was no significant difference between these values.

The disappearance of the trivalent species with time, when stored at both 40 and 60ºC, could be due to oxidation to the pentavalent form, as it has been previously discussed in section 3.1. It has been shown that Sb (III) is easily oxidized to Sb (V) within a short time at low concentrations (Filella, Belzile & Chen, 2002b; Miravet, López-Sánchez & Rubio, 2004; Miravet, Bonilla, López-Sánchez & Rubio, 2006b).

The results clearly show that at storage temperatures of 40ºC and 60ºC, Sb migration from PET to drinking water accelerates over time. This effect can be attributed to the degradation of PET with temperature. Degradation by thermo-oxidative and/or thermo-mechanical processes at temperatures higher than 250ºC is well known (Romao, Franco, Corilo, Eberlin, Spinacé & De Paoli, 2009) but has also been described at 40ºC. According to X-ray absorption fine structure (XAFS) measurements, the leaching behaviour of Sb into drinking water after 45 days at 40ºC is mainly due to the degradation of PET (Takahashi et al., 2008).

However, additional variables can also affect the migration behaviour. Total Sb concentration in PET, bottle volume and wall thickness, activation energy and diffusion coefficients of Sb were used in a mathematical model for calculating migration with temperature and time by Welle et al. (2011). Even if experimental values obtained in this work at room temperature and 40 ºC are slightly lower than those proposed by this model, the tendency up to 220 days is comparable. No data at 60ºC are available in Welle's study (Welle et al, 2011).

Migration behaviour is also dependent on the type of water (Bach et al., 2013). As all samples were non-carbonated waters, this parameter was not studied in this paper and future investigations will be focused on the effect of the type of sample in migration behaviour.

4. Conclusions

Although the concentration of Sb in PET material used for water bottling was between 191 and 268 mg kg^{-1}, only small quantities of antimony were released from the plastic into the water.

Significant amounts of Sb migrated into the water when bottles were stored at 60ºC and remained in the water matrix once they had been released.

Migration of antimony from the plastic into the mineral water gives rise to concentrations under the maximum allowed by the EU at storage temperatures below 60ºC, whereas at 60ºC Sb migration is more rapid and the limit is exceeded in 15 days.

After migration experiments, Sb(V) was the predominant species in the measured extracts. Although the most toxic species, Sb(III), was also present at 40 and 60ºC from the fiftieth and the third day, respectively, its presence decreased onwards due to the oxidation of Sb(III) to Sb(V).

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FIGURE CAPTIONS

Figure 1. Total Sb and Sb (V) concentration (μg L^{-1}) in bottled mineral water samples from three different-coloured PET brands. Sb (III) was not detected at day 0 and was not quantified thereafter. Times and temperature are mentioned for each brand. Legend for bottle colours: CL: clear; LB: light blue; DB: dark blue. LD Sb total = 0.11 μg L^{-1}; LQ Sb total = 0.14 μg L^{-1}; LD Sb (V) = 0.05 μg L^{-1}; LQ Sb (V) = 0.16 μg L^{-1}; LD Sb (III) = 0.25 μg L^{-1}; LQ Sb (III) = 0.83 μg L^{-1}.

Figure 2. Evolution of total Sb in bottled drinking water stored at 40 and 60ºC for 220 days. Legend for bottle colours: CL: clear; LB: light blue; DB: dark blue.

Figure 3. Evolution of Sb (V) in bottled drinking water stored at 40 and 60ºC for 220 days. Legend for bottle colours: CL: clear; LB: light blue; DB: dark blue.

Figure 4. Chromatograms obtained from samples stored at 60ºC by HPLC-ICP-MS at days 0, 7, 50 and 97. The insert shows the chromatograms obtained at days 0 and 7, indicating the presence of Sb (III).

TABLE TITLES

Table 1. Total antimony concentration and speciation in PET.

Table 2. Leaching of antimony (III) from PET into water samples stored at 60ºC for 50 to 220 days.

Table 1

Total antimony concentration and speciation in PET.

Samples	Sb total[a] (mg kg^{-1})	Sb total[b] (µg kg^{-1})	Sb (V)[b] (µg kg^{-1})	Sb (III)[b] (µg kg^{-1})
CL	203 ± 1.4 (0.7%)	11.1 ± 1.4 (12.4%)	8.6 ± 1.4 (16.4%)	< LD
LB	191 ± 2.7 (1.4%)	18.2 ± 2.1 (11.4%)	16.5 ± 2.7 (16.4 %)	< LD
DB	268 ± 2.0 (2.0%)	10.0 ± 1.5 (14.7%)	6.6 ± 0.4 (6.8%)	< LD

[a] Concentrations obtained by microwave digestion. Results are expressed as mean Sb value ± Standard Deviation in mg kg^{-1} (n = 3).

[b] Concentrations obtained by HCl extraction. Results are expressed as mean Sb value ± Standard Deviation in µg kg^{-1} (n = 3).

Samples were clear (NB), light blue (LB) and dark blue (DB). The relative standard deviations are expressed in % in parentheses. LD Sb total HCl extraction = 2.29 µg kg^{-1}; LQ Sb total HCl extraction = 2.92 µg kg^{-1}; LD Sb (V) = 0.5 µg kg^{-1}; LQ Sb (V) = 1.6 µg kg^{-1}; LD Sb (III) = 2.5 µg kg^{-1}; LQ Sb (III) = 8.3 µg kg^{-1}.

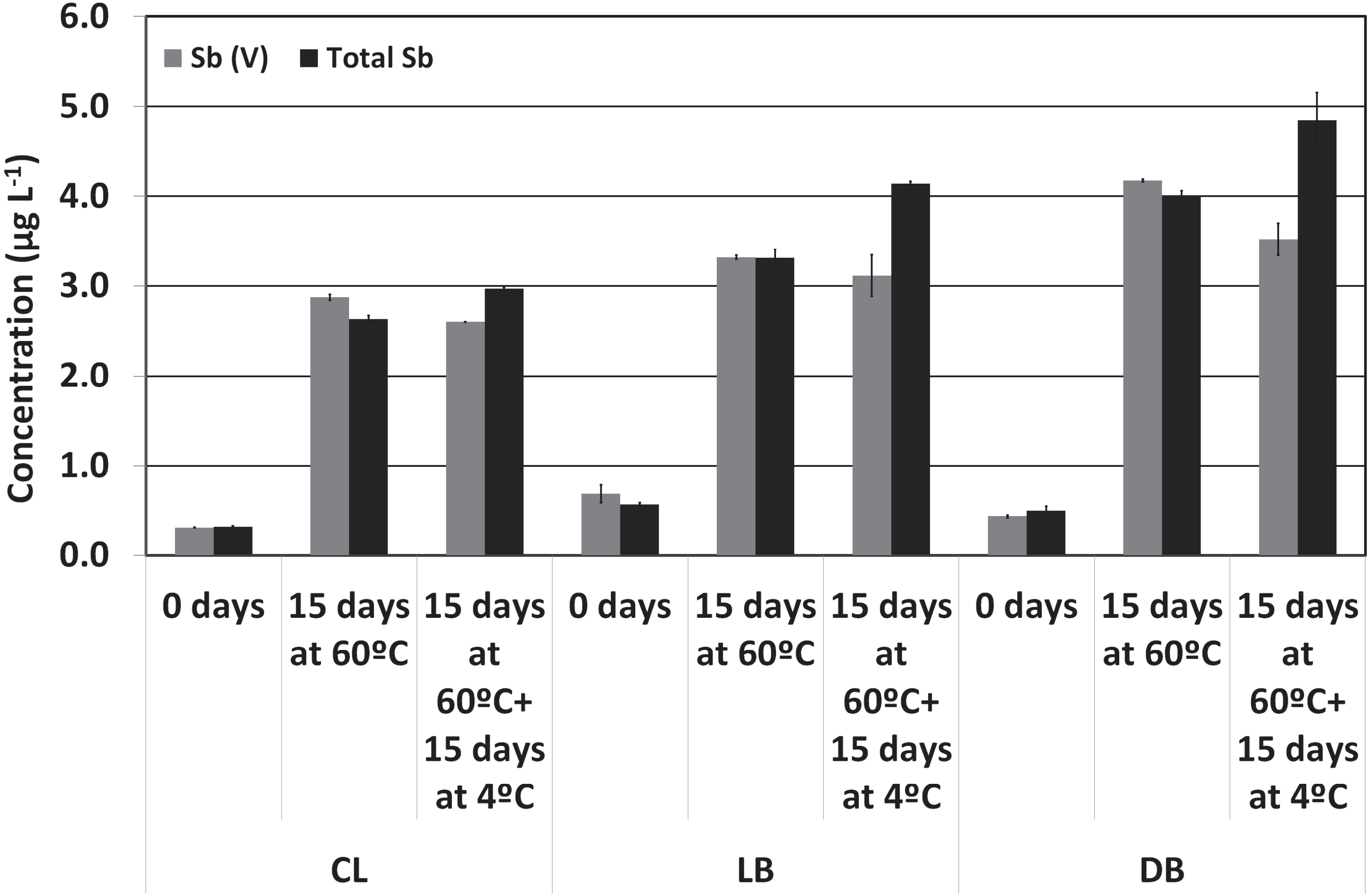
Table 2

Leaching of antimony (III) from PET into water samples stored at 60ºC for 50 to 220 days.

Sample	Day 50	Day 68	Day 78	Day 97	Day 135	Day 220
CL	0.90 ± 0.12	1.93 ± 0.07	2.04 ± 0.09	1.90 ± 0.11	2.76 ± 0.10	1.17 ± 0.13
LB	0.86 ± 0.21	1.99 ± 0.28	1.53 ± 0.20	0.85 ± 0.26	< LD	< LD
DB	5.61 ± 0.69	7.10 ± 0.35	7.12 ± 0.34	6.63 ± 0.34	5.91 ± 0.67	3.74 ± 0.34

The concentration is in µg L^{-1}. Samples were stored in clear (NB), light blue (LB) and dark blue (DB) bottles.

613 Figure 1



614

Figure 2

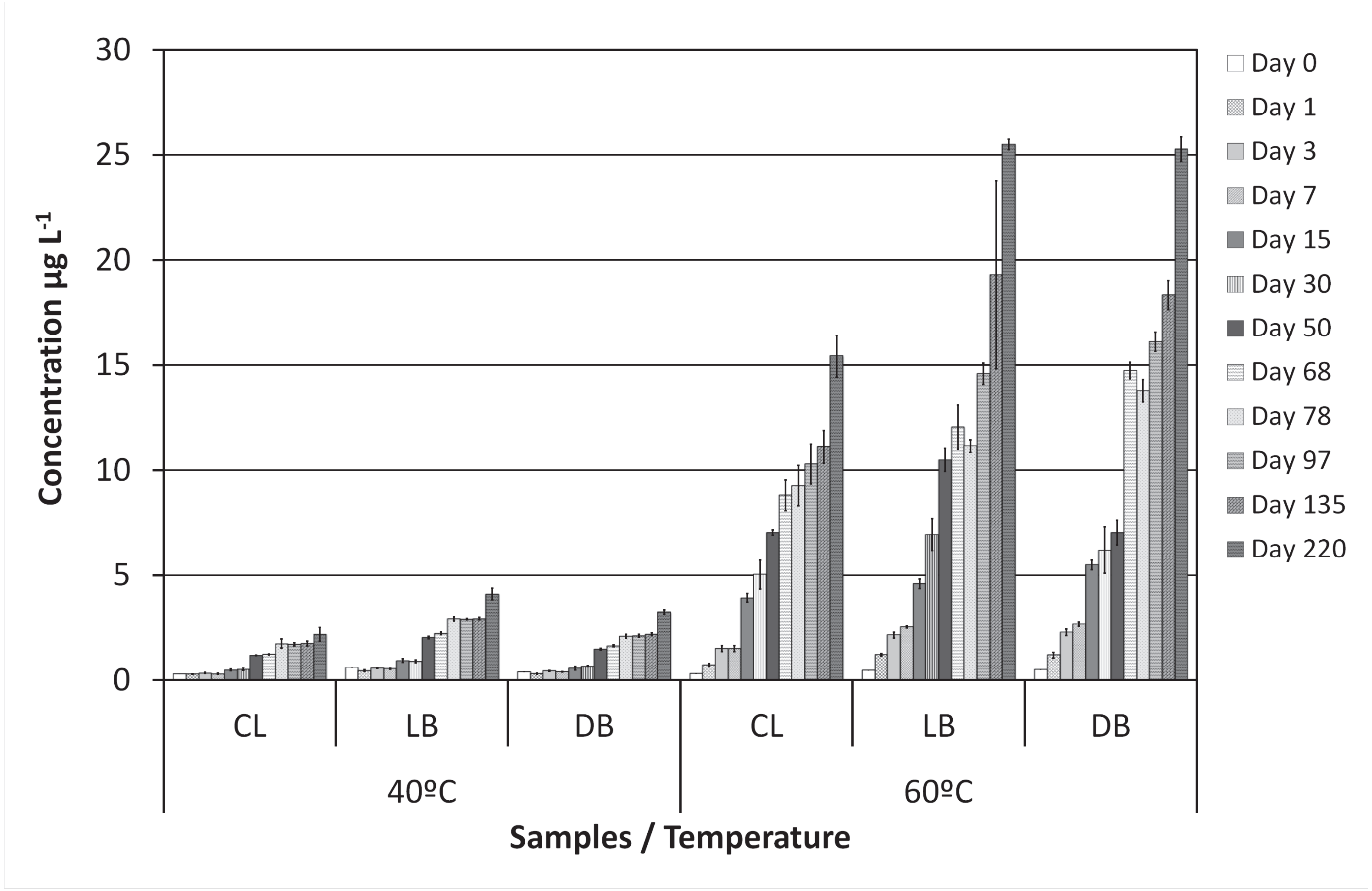
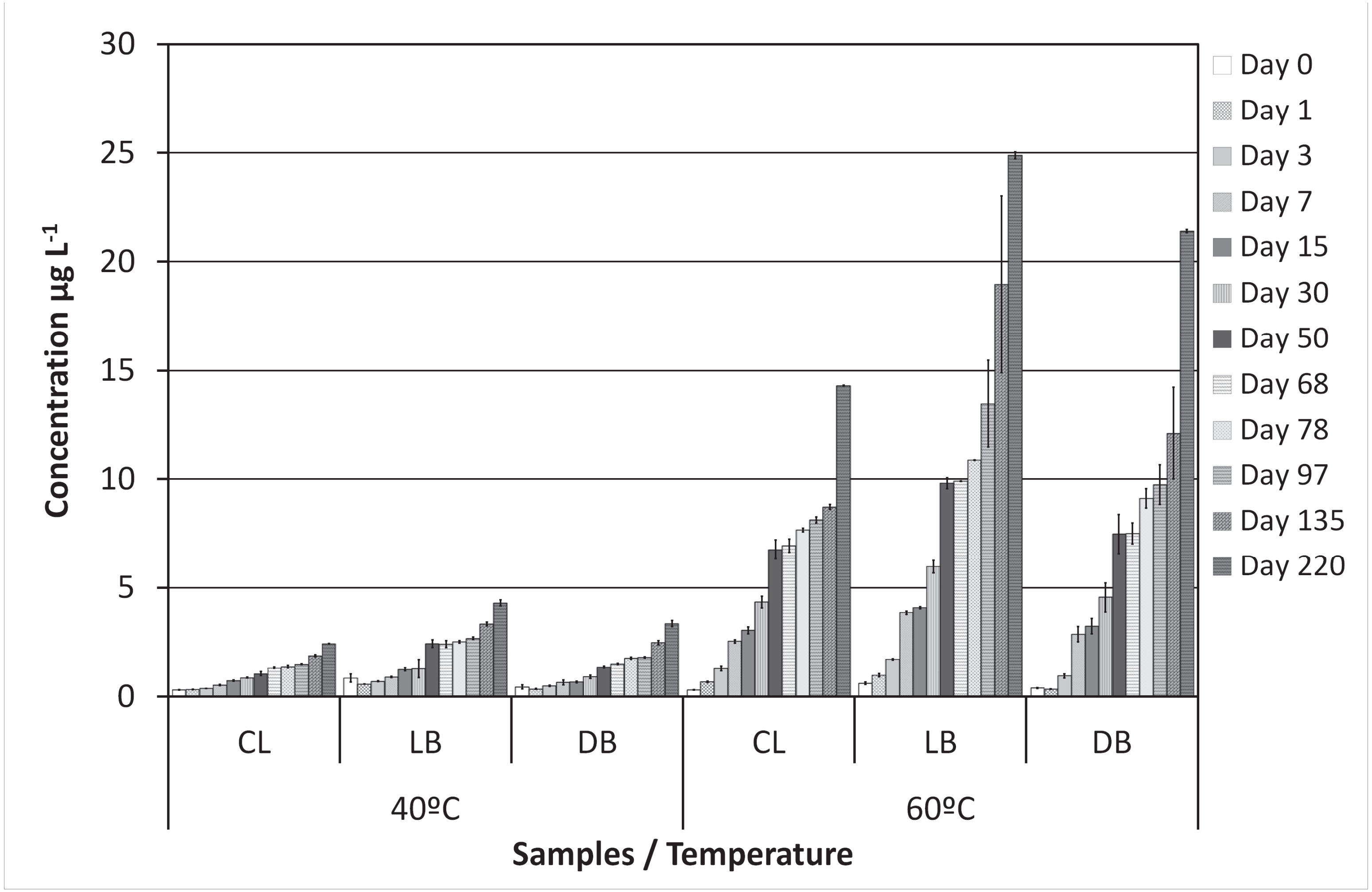

30
25
20
15
10
5
0
Concentration µg L-1
CL
LB
DB
CL
LB
DB
40ºC
60ºC
Samples / Temperature
Day 0
Day 1
Day 3
Day 7
Day 15
Day 30
Day 50
Day 68
Day 78
Day 97
Day 135
Day 220

Figure 3



Concentration µg L-1
30
25
20
15
10
5
0
CL
LB
DB
CL
LB
DB
40ºC
60ºC
Samples / Temperature
Day 0
Day 1
Day 3
Day 7
Day 15
Day 30
Day 50
Day 68
Day 78
Day 97
Day 135
Day 220